

# Measuring methane and its isotopes $^{12}\text{CH}_4$ , $^{13}\text{CH}_4$ , and $\text{CH}_3\text{D}$ on the surface of Mars with *in situ* laser spectroscopy

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In light of the recent discovery of methane on Mars and its possible biological origin, a strategy is described for making *in situ* measurements of methane and its isotopes on the surface of Mars by laser spectroscopy in the 3.3- $\mu\text{m}$  wavelength region. An instrument of reasonable mass ( $\sim 1$  lb) and power (few watts) is capable of measuring mixing ratios down to 0.1 part per  $10^9$  by volume, a hundred times lower than recently reported observations. Making accurate measurements of  $^{13}\text{CH}_4$  and  $\text{CH}_3\text{D}$  will be more difficult. For measuring  $\delta^{13}\text{C}$  to 10‰ and  $\delta\text{D}$  to 50‰, sample preconcentration will be required to  $\sim 3$  parts per  $10^6$  by volume for  $\delta^{13}\text{C}$  and to  $\sim 40$  parts per  $10^6$  by volume for  $\delta\text{D}$ . This need would be mitigated by the discovery of larger local abundances of methane near the source regions. © 2005 Optical Society of America

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## 1. Introduction

### A. Observations of $\text{CH}_4$ on Mars

It has long been postulated that, as evidenced on Earth, a biosphere on Mars may reveal itself through release of biogenic gases such as  $\text{CH}_4$ ,  $\text{COS}$ ,  $\text{H}_2\text{S}$ ,  $\text{NH}_3$ , and  $\text{N}_2\text{O}$ .<sup>1,2</sup> The discovery of microbial communities in Earth's extreme environments<sup>3</sup> has increased the possibility of such communities on Mars despite the recognition by Viking Lander studies<sup>2</sup> of the harsh surface environment. Only weeks after the successful landing and operation of the Mars Exploration Rover twins Spirit and Opportunity, ground-based observations of Mars made years earlier with a Fourier-transform infrared spectrometer at the Canada–France–Hawaii Telescope have detected methane in the Martian atmosphere by use of the *P*-branch region near a 3.3- $\mu\text{m}$  wavelength. Observed mixing ratios of  $10 \pm 3$  parts per  $10^9$  by volume (ppbv) (Ref. 4) are consistent with the confirmed results from the Planetary Fourier Spectrometer onboard the Euro-

pean Space Agency's Mars Express currently in orbit.<sup>5</sup> This is an extremely important discovery that will effect future strategies for Mars exploration.<sup>6</sup>

Rapidly oxidized to  $\text{H}_2\text{O}$  and  $\text{CO}_2$ ,  $\text{CH}_4$  has a relatively short lifetime on Mars ( $\sim 300$  years)<sup>7</sup> and must be constantly replenished to maintain any presence in the atmosphere, even at low concentrations. Two possible sources are being considered<sup>4,5,7</sup>: volcanic and hydrothermal activity (thermogenic) and microbial activity (biogenic). In the former,  $\text{CH}_4$  is produced in subsurface reactions involving water. In the latter, microbes convert  $\text{CO}_2$  to  $\text{CH}_4$  in a process known as methanogenesis.<sup>8</sup> Scientists from both ground-based and orbiter observations conclude that methanogenesis by living subterranean organisms is a plausible explanation, although Martian biota would be scarce and highly localized, possibly confined to oasis regions.<sup>4,5,7</sup>

### B. Isotope Ratios for Identifying Biogenic Methane

Ratios of carbon's two stable, naturally occurring isotopes  $^{12}\text{C}$  (98.89%) and  $^{13}\text{C}$  (1.11%) are expressed in parts per thousand (‰) relative to the standard Vienna Pee Dee Belemnite.<sup>9</sup> For example,

$$\delta^{13}\text{C} = [(^{13}\text{C}/^{12}\text{C})_{\text{sample}} / (^{13}\text{C}/^{12}\text{C})_{\text{standard}} - 1] \times 1000\text{‰}. \quad (1)$$

On Earth, inorganic carbon sediments such as lime-

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Table 1. Variation in Methane Isotope Ratios

| Sources  | $\delta^{13}\text{C}$              | $\delta\text{D}$                    |
|--|------------------------------------|-------------------------------------|
| Earth  |                                    |                                     |
| Inorganic  | $\sim 0\text{‰}$ VPDB <sup>a</sup> | $\sim 0\text{‰}$ SMOW               |
| Biogenic   | $-60 \pm 5\text{‰}$                | $-310 \pm 20\text{‰}$               |
| Fossil   | $-40 \pm 8\text{‰}$                | $-160 \pm 40\text{‰}$               |
| Biomass burning (20% C <sub>4</sub> and 80% C <sub>3</sub> plants) | $-24 \pm 3\text{‰}$                | $-225 \pm 30\text{‰}$               |
| Mean biological values on Earth                                    | $-40 \pm 20\text{‰}$               | $-200 \pm 100\text{‰}$              |
| Expectation on Mars  |                                    |                                     |
| Inorganic  | $\sim 0\text{‰}$ VPDB <sup>a</sup> | $\sim 0\text{‰}$ (4500‰ SMOW)       |
| Biological   | $-40 \pm 20\text{‰}$               | $-200 \pm 100\text{‰}$ (3400‰ SMOW) |

<sup>a</sup>Vienna Pee Dee Belemnite.

stone have a  $\delta^{13}\text{C}$  of  $\approx 0\text{‰}$ , and atmospheric  $\delta^{13}\text{C}$  is approximately  $-7\text{‰}$ . Photosynthetic organisms preferentially take up  $^{12}\text{C}$  over  $^{13}\text{C}$  because of faster diffusion through leaf stomata and enzymatic preference, producing a kinetic isotopic shift in  $\delta^{13}\text{C}$  of approximately  $-13\text{‰}$  for C<sub>4</sub> plants (e.g., salt marsh, tropical grasses, sugar cane) and  $-27\text{‰}$  for C<sub>3</sub> plants (wheat, rice, soybean, sugar beet, most plants).<sup>10</sup> Isotopic differences can be propagated in the food chain, with small additional fractionation possibly occurring at each stage. These isotope ratios characterize organic sediments compared with that of inorganic carbonate in sedimentary rocks.<sup>11</sup> This organic carbon depleted in  $^{13}\text{C}$  is retained at burial. For example, ancient sediments can be identified as biological through their observed depletion in  $^{13}\text{C}$  relative to inorganic carbon and provide an estimate of the age of life on Earth (see the discussion in Ref. 1; stromatolites are carbonate formations deposited on cyanobacteria mats from a combination of both bacterial and sedimentary processes, mainly the latter, and show little depletion). Isotopic exchange between aqueous carbonate and atmospheric CO<sub>2</sub> results in enrichment of  $^{13}\text{C}$  in carbonates.

Short of identifying microbial communities or locating methane-producing sources through flux measurements, distinction between biogenic and abiogenic sources of methane can be made by careful measurement of its isotopic composition, namely, the ratios of  $^{13}\text{CH}_4/\text{CH}_4$  and  $\text{CH}_3\text{D}/\text{CH}_4$ , since life forms preferentially use the lighter isotope in taking in and expelling products<sup>12</sup> and therefore show distinct variations in isotopic content.

In Earth's atmosphere, methane is an important contributor to greenhouse warming and plays a central role in the chemistry of the troposphere as a sink for OH radicals and in the stratosphere as a source for water.<sup>13</sup> Atmospheric methane abundances since preindustrial times have more than doubled,<sup>14</sup> mainly because of anthropogenic contributions to increases in its principal sources: natural wetlands (22%); rice paddies (21%); enteric fermentation (animals) (15%); gas drilling, venting, transmission (9%); biomass burning (8%); termites (8%); landfills (8%); coal mining (7%); oceans (2%); freshwaters (1%); and hydrate destabilization (1%).<sup>14,15</sup>

Most methane on Earth is produced by biological sources, either by current microbial activity or from activity from long ago that produced underground sources of natural gas. These sources can be categorized<sup>15</sup> as biogenic, fossil, and biomass burning. Biogenic sources on Earth produce CH<sub>4</sub> directly from contemporary bacterial action (rice paddies, animals, wetlands, and landfills) with the characteristic isotope ratios given in Table 1. Notably, some bacterial that generate methane during methanogenesis produce methane with  $\delta^{13}\text{C}$  values as high as  $-110\text{‰}$ .<sup>16</sup> Also, methane hydrate deposits found on the seafloor in the Gulf of Mexico<sup>17</sup> have  $\delta^{13}\text{C}$  values of  $-70\text{‰}$ , in accord with its biogenic origin. Methane is lost through reaction with OH, Cl, and O(<sup>1</sup>D) and consumption by soil or oceanic bacteria. Atmospheric CH<sub>4</sub> is slightly enriched in  $^{13}\text{C}$  because of the kinetic isotope effect that favors reaction of OH with  $^{12}\text{CH}_4$  over  $^{13}\text{CH}_4$ .<sup>14</sup> These bacterial influences on isotopic ratios<sup>18</sup> are more relevant for Mars than those of plants.

The D/H ratio is an important indicator of the origin and history of water since it can increase as a planet loses hydrogen to escape when solar wind protons provide kinetic energy through collision. The D/H ratio of Earth ( $\sim 1.54 \times 10^{-4}$ ) is considered higher than that expected ( $8 \times 10^{-5}$ ) for water condensed at Earth's distance, demonstrating a connection between the solar system and interstellar water (D/H ratios  $> 10^{-3}$ ). On Earth, local processes of condensation and evaporation produce large changes.<sup>19</sup> For Mars, its magnetic field is not strong enough to deflect solar particles, and large amounts of H have been lost over time, producing a D/H ratio  $\approx 5.5$  times that of Earth.<sup>20</sup> Because water can also leave Mars by thermal or Jeans escape, or by impact erosion, this implies that the original water reservoir on Mars was several—perhaps up to 100-times its present size, assuming exchange with the atmosphere. Thus methane sources on Mars are expected to contain at least five times the amount of CH<sub>3</sub>D relative to CH<sub>4</sub> to produce a D/H ratio ( $[\text{CH}_3\text{D}]/4[\text{CH}_4]$ ) five times that of Earth. The calculation of  $\delta\text{D}$  is expressed as the D/H ratio of the sample with respect to that of water. For Earth,

Table 2. Needed Methane Amounts for Required Precisions

| Measurement                 | Methane Amount Needed                | Preconcentration Factor<br>from 10 ppbv | Notes                      |
|-----------------------------|--------------------------------------|---|----------------------------|
| CH <sub>4</sub> to 0.1 ppbv | Ambient levels greater than 0.1 ppbv | None needed                             | Open path or cell sampling |
| δ <sup>13</sup> C to 10‰    | ~3 ppmv                              | 300                                     | Cell only                  |
| δD to 50‰                   | ~40 ppmv                             | 4000                                    | Cell only                  |

$$\delta D = [(D/H)_{\text{sample}} / (D/H)_{\text{standard}} - 1] \times 1000\text{‰}, \quad (2)$$

and D/H ratios are expressed relative to standard mean ocean water (SMOW).<sup>9</sup> For methane,

$$\delta D = \{([CH_3D]/4[CH_4]) / ([HDO]/2[H_2O]) - 1\} \times 1000\text{‰}. \quad (3)$$

Natural abundances of these isotopic gases produce δD values close to 0‰ on Earth (with biogenic variations close to ~200‰). Strictly, the higher D/H ratio of Mars would produce δD values of typically 4500‰. If as on Earth biological processes on Mars effect the methane D/H values by a similar 20%, then δD values of ~3400‰ would be expected. To avoid this unnecessary confusion in standards notation, we report δD values in a similar way to Earth (Table 2).

On Earth, then, we can readily distinguish biogenic methane from other sources using its isotopic content of <sup>13</sup>C/<sup>12</sup>C and D/H ratios. As described in a series of papers by Bergamaschi *et al.*,<sup>21–23</sup> methane isotope ratios can be used to discriminate both source and sink terms. For example, seasonal cycle and synoptic-scale variations show δD in phase with CH<sub>4</sub>, with a kinetic isotope effect consistent with OH removal, whereas variations of δ<sup>13</sup>C are out of phase and show a contribution from seasonally varying sources.<sup>23</sup> However, we caution here that CH<sub>3</sub>D/CH<sub>4</sub> ratios on Earth are not dominated by fractionation due to uptake by methanogens, but rather by the evaporation rates of the water in which they live.<sup>8</sup>

On Mars, as pointed out by McKay *et al.*,<sup>1</sup> it is uncertain that Martian enzymes that fix CO<sub>2</sub> from the atmosphere would produce the same isotope shift as observed on Earth. Considering the ready abundance of substrate, and the nature of enzymatic processes, it is highly likely that a significant difference would exist between organic and inorganic carbon and that methane gas produced from biological processes would be significantly depleted in δ<sup>13</sup>C. Although subterranean methanogenesis on Mars would produce significant depletion in δ<sup>13</sup>C, it is not clear that it would produce the expected five times enhancement of D/H since the CH<sub>3</sub>D/CH<sub>4</sub> ratio depends also on the bacterial supply environment.

#### C. Measurement Requirements for Earth and Mars

Measurement requirements for methane and its isotopes depend specifically on the application. Measuring methane itself on Earth is relatively straightforward because of its relatively high mixing ratio

[~1.7 parts per 10<sup>6</sup> by volume (ppmv)].<sup>13</sup> Obtaining measurements with precisions of ~0.1% and absolute accuracy of ~3% is achieved routinely with aircraft and balloon laser spectrometers at 3.3 and 7.5 μm.<sup>23–27</sup> Discriminating the sources and sinks of atmospheric methane and seasonal and spatial variations requires measurement of isotope ratios to better than 0.1‰ for δ<sup>13</sup>C and to better than 2‰ for δD. Sensitivities at these levels have been achieved with tunable laser and mass spectrometric techniques.<sup>15</sup> On Earth, then, maturity of the science questions and the high mixing ratios has helped increase isotopic measurement capability.

For Mars, a different approach is needed. First, there is very little (10 ppbv) methane in the atmosphere, so high-accuracy measurement of methane alone is challenging. It follows that isotopic measurements will be difficult to undertake with optical methods. However, the isotopic measurement requirements are relaxed to some extent at this early phase of basic discovery. To improve on these initial observations, measurements of CH<sub>4</sub> in the atmosphere must be made at precisions and accuracies better than 1 ppbv, and preferably to 0.1 ppbv. To provide a basic distinction between biogenic and abiotic sources on Mars, we suggest that isotope ratios in methane would have to be made to better than 10‰ (preferably 5‰) for δ<sup>13</sup>C and to better than 50‰ for δD.

#### D. Tunable Laser Spectroscopy

Tunable laser absorption spectroscopy is widely recognized as a direct, noninvasive, simple measurement technique that is known for its high sensitivity (subparts per 10<sup>9</sup>) and specificity.<sup>28</sup> Using wavelength-modulation techniques, minimum-detectable absorptions as small as 2 parts in 10<sup>6</sup> are possible, with 2 parts in 10<sup>5</sup> readily achieved in flight experiments. For reasonable path lengths, this translates to subparts per 10<sup>9</sup> sensitivities for numerous species in the mid infrared and tens of parts in 10<sup>9</sup> in the near-IR region. These numbers depend specifically on the gas and conditions of interest. Because of its flammability and explosive potential, methane is considered an important safety hazard whose detection and monitoring is of interest for several industrial applications, including natural and liquefied gas handling, storage, pipeline transport, and coal mining. Methane is also important in combustion diagnostics and diamond vapor deposition. The scientific and industrial interest in methane has led to a wide variety of detection applications that are either mass spectrometric or optical. Laser-based detection has



included the first *in situ* atmospheric measurements of  $\text{CH}_4$  and  $^{13}\text{CH}_4$  in 1988 (Ref. 29) with tunable diode laser (TDL) measurements; near-IR 1.65- $\mu\text{m}$  TDL measurements<sup>30,32</sup>; mid-IR measurements at 3.4  $\mu\text{m}$  with lead salt TDLs<sup>26</sup>; quantum-cascade (QC) laser measurements at 8  $\mu\text{m}$  in the laboratory<sup>32</sup> and Earth's atmosphere<sup>24</sup>; difference-frequency generation for methane<sup>33</sup> and  $\text{CH}_3\text{D}$  measurement<sup>34</sup>; and isotopic measurements with a CO overtone sideband laser with cavity leak-out spectroscopy.<sup>35</sup>

#### E. Optical versus Mass Spectrometric Methods of Measurement

Tunable laser absorption offers several advantages over mass spectroscopy for measurement of gases *in situ* at low concentrations. The measurements are direct, noninvasive, and can be made very fast (e.g., tens of hertz for flux studies) if the signal-to-noise ratio permits. The measurement is simple and self-calibrating in laser power through Beer's law. Direct calibration with standard gases is easy and unambiguous. Laboratory studies can be made with excess of gases to avoid spectral interferences. For planetary applications, the instrumentation is simple, easily miniaturized in size, and has low mass and power. Thus, to measure water in the Martian atmosphere, a Mars laser hygrometer based on a near-IR TDL can determine water mixing ratios down to 0.1 ppmv in an instrument with a total (optical head, electronics, cabling) mass of only 230 g.<sup>36</sup> For some gases (e.g.,  $\text{H}_2\text{O}$ ,  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{O}_2$ , and  $\text{CH}_4$ ) on Mars, tunable laser spectroscopy is the preferred choice given the limitations on size, complexity, mass, and power.

For isotope ratios, however, there is no doubt that mass spectrometers are capable of making more precise and accurate measurements than optical methods. In specific cases mass spectrometry is limited by mass equivalence, or by indirect sample preparation procedures, so that optical (laser) methods would offer distinct advantages. Unlike mass spectrometers, high-resolution laser spectroscopy used with isolated vibration-rotation lines can distinguish between isotopic species of the same mass (e.g.,  $^{14}\text{N}^{15}\text{NO}$  and  $^{15}\text{N}^{14}\text{NO}$ ,  $\text{CH}_3\text{D}$  and  $^{13}\text{CH}_4$ ,  $\text{HDO}$  and  $\text{H}_2^{17}\text{O}$ ). In particular, for  $\text{CH}_3\text{D}$  in methane, mass spectrometers cannot resolve the small mass difference of 0.003 amu between  $\text{CH}_3\text{D}$  and  $^{13}\text{CH}_4$  and must resort to chemical conversion.

Mass spectrometric techniques used to measure methane isotopic composition are complicated and are usually based on conversion of  $\text{CH}_4$  to  $\text{CO}_2$  that is then isotopically analyzed. Typically,<sup>37</sup> liquid-nitrogen cryotrapers are used to first remove  $\text{CO}_2$ ,  $\text{N}_2\text{O}$ , and  $\text{H}_2\text{O}$  (note that  $^{14}\text{N}_2^{16}\text{O}$  has the same mass as parent  $\text{CO}_2$ ). The airstream is then passed through the Schutze reagent  $\text{I}_2\text{O}_5$  to oxidize  $\text{CO}$  to  $\text{CO}_2$ , which must also be removed by a liquid-nitrogen trap. Finally, any  $\text{CH}_4$  in the sample is oxidized to  $\text{CO}_2$  through a platinized silica oven at  $\sim 800^\circ\text{C}$ , and the  $\text{CO}_2$  is collected on a liquid-nitrogen trap and cryogenically distilled from  $\text{H}_2\text{O}$  before analysis.<sup>15,37</sup>

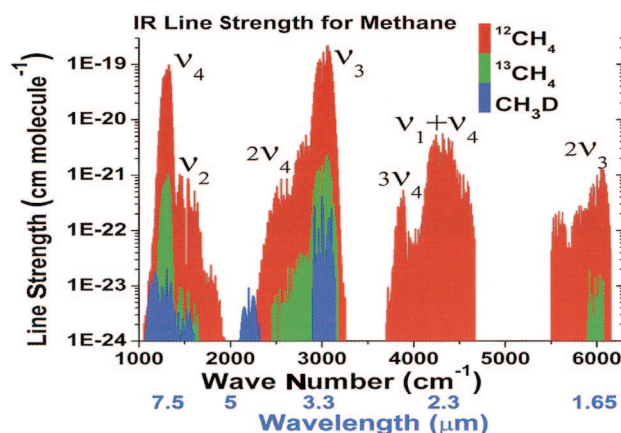


Fig. 1. Vibration-rotation line positions and intensities that make up the main absorption band regions, as provided by the HITRAN 2000 line listing.<sup>39</sup>

When large gas abundances are available, precisions of 0.05‰ for  $\delta^{13}\text{C}$  in methane are achieved, with accuracies of  $\approx 0.1\%$ .<sup>23</sup> To overcome the difficulties of measuring  $\text{CH}_3\text{D}$ , mass spectrometric methods must first subject the methane sample to catalytic oxidation to  $\text{CO}_2$  and water, reduction of the water produced to  $\text{H}_2$  and  $\text{HD}$ , and determination of the hydrogen  $\delta\text{D}$  values.<sup>23</sup> Uncertainties of 5‰ for  $\delta\text{D}$  values are typical for mass spectrometry. Of more relevance to Mars application, mass spectrometers have to overcome two additional difficulties of measurement. First, conversion of minute amounts of methane to  $\text{CO}_2$  may be compromised by the difficulty in fully scrubbing the Mars atmospheric sample of its main constituent,  $\text{CO}_2$ . In addition, hydrogen is often a remnant gas in a clean mass spectrometer that reacts with carbon diffusing out of hot filaments to actually produce methane gas, especially at low abundances.

## 2. Infrared Spectroscopy of $\text{CH}_4$

### A. Identifying Optimal Regions for $\text{CH}_4$ Detection and Isotope Ratio Determinations

Despite its simple molecular structure, methane has an extremely complex IR absorption spectrum that defies analysis based on a simple spherical rotor ( $\text{CH}_4$ ) or asymmetric rotor ( $\text{CH}_3\text{D}$ ) descriptions. Perturbation of energy levels and band interaction is the norm in methane,<sup>38</sup> so that even its simplest region near 7  $\mu\text{m}$  must be described by a simultaneous modeling of its two lowest fundamentals  $\nu_2$  and  $\nu_4$ . Figure 1 shows the vibration-rotation line strengths<sup>39</sup> in the region from 1.5 to 8  $\mu\text{m}$ . The main features of the absorption spectrum arise from sets of states that are described as polyads of interacting bands: at 7  $\mu\text{m}$ , the dyad ( $\nu_2$  and  $\nu_4$ ); at 3.5  $\mu\text{m}$ , the pentad ( $\nu_1$ ,  $\nu_3$ ,  $2\nu_4$ ,  $2\nu_2$ , and  $\nu_2 + \nu_4$ ); and at 2.3  $\mu\text{m}$ , an octad of bands made up of a variety of contributing overtone and combination bands.<sup>38</sup>

For detection of methane and its isotopes, we therefore identify four candidate spectral regions, in order

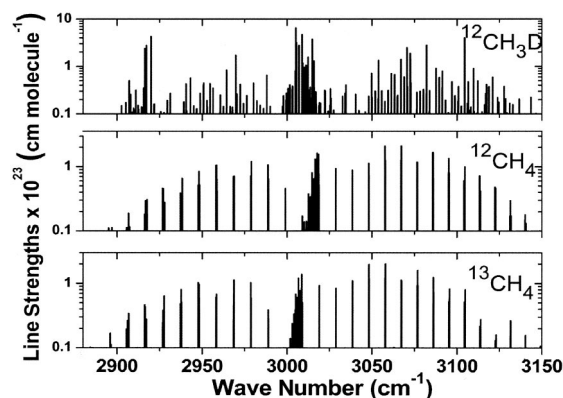


Fig. 2. Comparison of line positions and strengths of  $^{12}\text{CH}_3\text{D}$ ,  $^{13}\text{CH}_4$ , and  $^{12}\text{CH}_4$  lines of the  $\nu_3$  bands, as calculated from the HITRAN 2000 line listings.<sup>39</sup> Note that these are line strengths, not absorption intensities that will show relative differences depending on the temperature and pressure.

of vibration-rotation line strengths, as near  $3.3\ \mu\text{m}$  ( $\nu_3$  region), near  $7.5\ \mu\text{m}$  ( $\nu_4$  region), and the two near-IR regions near  $2.3$  and  $1.65\ \mu\text{m}$ .

Isotope ratio measurements performed with individual rovibrational lines can be made with better precision when adjacent lines of similar intensity can be used. Because both  $^{12}\text{CH}_4$  and  $^{13}\text{CH}_4$  are spherical rotors, they show similar vibrational-rotational line patterns that are shifted by  $\sim 10\ \text{cm}^{-1}$  due to the C mass difference (see Fig. 2). Therefore the location of the strongest  $^{13}\text{CH}_4$  isotopic lines will be relatively close to those of the parent  $^{12}\text{CH}_4$  species (i.e., *P*- and *R*-branch lines), and the isotopic ratio measurement will be effected by the large dynamic range ( $\sim 100$ ) expected for the different isotopic abundances. To compensate for the different intensity ratios, path lengths differing by a factor of 100 could be used,<sup>40,41</sup> but the isotopic ratio measurement may be somewhat effected, this time by the need to ratio different spectra. Alternatively, as pointed out by Bergamaschi *et al.*,<sup>21</sup> in the *Q*-branch region near  $3000\text{--}3010\ \text{cm}^{-1}$  (Fig. 2), strong  $^{13}\text{CH}_4$  lines of comparable absorption intensity to weak  $^{12}\text{CH}_4$  lines can be found. In selecting suitable line pairs, caution is given regarding the possible large dependencies that a ratio in intensity has on the temperature dependence through ground-state energies and temperature-dependent broadening coefficients.

#### B. Laser Source Availability at Suitable Wavelength Regions

Selection of an optimal wavelength region for gas measurement is application specific and is based on a variety of parameters that includes strength of absorption, avoidance of spectral interferences from other gases, availability of laser sources, and the detection requirements. In general, continuous-wave (cw), single-mode distributed feedback laser sources are preferred over pulsed sources because of the superior detection limits that are associated with continuous detection methods (phase-sensitive detection

by use of second-derivative detection or fast, integrated rapid scan), narrow laser linewidths (tens of megahertz), and high output powers (milliwatts).

For planetary applications, both TDL and QC laser sources can be considered, but cryogenic cooling is not possible, so thermoelectrically cooled devices must be used. Room-temperature (TE cooler) TDL sources of high spectral purity (single mode) and high output powers ( $5\text{--}50\ \text{mW}$ ) are now available in the near-IR region where molecules like  $\text{H}_2\text{O}$  and  $\text{CO}_2$  have sufficiently strong IR absorption cross sections and are in considerable abundance (e.g., on Mars) to make measurement possible. Specifically, for wavelengths in the  $1\text{--}2\text{-}\mu\text{m}$  range, the MicroDevices Laboratory (MDL) at the Jet Propulsion Laboratory has produced single-mode distributed feedback devices that have been tested and flight qualified for the Mars Volatiles and Climate Surveyor Lander payload of the Mars 98 Surveyor mission: one for measurement of atmospheric and evolved  $\text{H}_2\text{O}$  at  $1.37\ \mu\text{m}$ .<sup>42</sup> Laser sources at  $1.87\ \mu\text{m}$  have also been made by both MDL and Nanoplus in Germany and are being flight qualified for future Mars missions. Until recently, TDL devices were available only in the range of  $1.3\text{--}2.1\ \mu\text{m}$ .

QC lasers are new mid-IR semiconductor laser sources (invented in 1994) that are fundamentally different from TDLs.<sup>43</sup> Rather than depend on the electronic bandgap of materials, the QC laser results from the application of quantum engineering of the electronic energy levels. Emission results from intersubband transitions within the conduction band of a cascaded InGaAs/InAlAs multiple quantum-well structure that were grown lattice matched to an InP substrate by molecular beam epitaxy,<sup>42</sup> with the output wavelength determined by quantum confinement (i.e., by the layers' thickness of the active region rather than by the bandgap of the material<sup>43</sup>). Progress in QC laser development has been rapid: Cryogenically cooled cw distributed feedback QC lasers have been flown on high-altitude aircraft to measure  $\text{CH}_4$  and  $\text{N}_2\text{O}$ ,<sup>24</sup> and room-temperature cw operation of QC lasers (at  $9\ \mu\text{m}$ ) has now been achieved<sup>44</sup> with cw output powers of a few milliwatts. QC lasers are readily available from  $\sim 5$  to  $12\ \mu\text{m}$ .

Until now, the important wavelength region between  $\sim 2$  and  $4\ \mu\text{m}$  could not be accessed by single laser devices, but only by difference-frequency laser systems.<sup>45</sup> A new approach to producing TDLs in the  $2\text{--}4\ \mu\text{m}$  region is being developed at MDL.<sup>46</sup> It is based on the fabrication of type-II interband cascade (IC) lasers in the versatile, but little-investigated Sb-based heterostructure system. IC lasers reuse injected electrons by taking advantage of the broken bandgap alignment in Sb-based type-II quantum wells to form cascade stages, leading to a quantum efficiency greater than the conventional limit of unity. These devices better cover the wavelength range of  $2.7\text{--}4.5\ \mu\text{m}$  where intersubband QC lasers have difficulty performing because of band offset limitations in the constituent materials. Also, type-II IC

laser designs can circumvent the fast phonon-scattering loss of intersubband QC lasers and suppress Auger recombination through band-structure engineering, resulting in a low-threshold current density with high-power conversion efficiency. These properties make mid-IR type-II IC lasers promising for the delivery of high output power even at relatively high operating temperatures. Theoretical calculations have suggested that type-II IC lasers can also operate in cw up to room temperature.<sup>46</sup> Recent efforts at MDL have achieved encouraging results. Observed performance metrics include pulsed operation at high temperatures up to 325 K and cw output power of >1 mW at 200 K, illustrating their great potential.

### 3. Previous Measurements on Earth

#### A. Methane Spectrometer Studies

A thorough study of laser-based measurements of methane and its isotopes for Earth applications has been made by Bergamaschi *et al.* in a series of papers<sup>21–23</sup> in which they assess precision and accuracies obtained from laboratory studies and analyze field measurements of Earth's troposphere. Using the stronger line pairs available for CH<sub>3</sub>D and <sup>13</sup>CH<sub>4</sub> near 3.3  $\mu$ m, these authors were able to produce  $\delta^{13}\text{C}$  and  $\delta\text{D}$  values at record precision and accuracy. By direct comparison with high-accuracy mass spectrometry, they achieved reproducibilities of 0.5‰ for  $\delta^{13}\text{C}$  and ~2‰ for  $\delta\text{D}$  using a multipass cell of 213-m path length at a pressure of tens of millibars. To reach this level of accuracy, ~50-ppmv methane (<sup>12</sup>CH<sub>4</sub>) in the sample gas was needed for  $\delta^{13}\text{C}$  and ~2000-ppmv methane (<sup>12</sup>CH<sub>4</sub>) for  $\delta\text{D}$ , with integration times of tens of minutes.

#### B. Aircraft Measurements of Methane and <sup>13</sup>CH<sub>4</sub>

Several tunable laser spectrometers measure CH<sub>4</sub> routinely at high precision and accuracy in Earth's atmosphere during aircraft campaigns that study photochemistry and dynamics, notably NASA Langley's differential absorption CO measurement instrument,<sup>25</sup> NASA Ames's Argus instrument,<sup>26</sup> the National Oceanic and Atmospheric Administration's methane spectrometer,<sup>27</sup> and Jet Propulsion Laboratory's aircraft laser infrared absorption spectrometer (ALIAS) instrument.<sup>28</sup> On 23 September 1999 the ALIAS instrument was flown in Earth's upper troposphere on NASA's ER-2 high-altitude aircraft, measuring CH<sub>4</sub> and its <sup>13</sup>CH<sub>4</sub> isotope using TDL spectroscopy of lines near 2927 cm<sup>-1</sup>. Typical atmospheric levels of methane sampled by ALIAS in an 80-m path length at 70 mbars were ~1.3 ppmv (<sup>12</sup>CH<sub>4</sub>). A study of achieved sensitivities during a 30-min portion of the flight showed that <sup>12</sup>CH<sub>4</sub> could be measured to a precision of ~2 ppbv in the measured 1300 ppbv. Although neighboring strong <sup>12</sup>CH<sub>4</sub> lines could be ratioed to precisions of ~0.2‰, the weak <sup>13</sup>CH<sub>4</sub> features produced measurements of  $\delta^{13}\text{C}$  that were precise to only ~5‰.

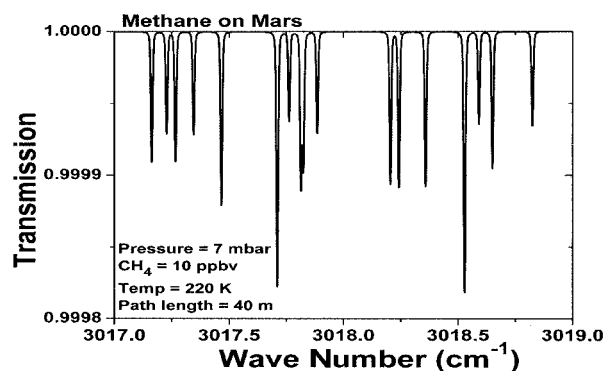


Fig. 3. Calculation of the transmission spectrum of a sample of 10-ppbv <sup>12</sup>CH<sub>4</sub> for Mars surface conditions of 7-mbar pressure, 220 K temperature, a path length of 40 m, and a laser linewidth of 20 MHz.

#### C. Laboratory Measurements of CH<sub>3</sub>D

In laboratory studies that used a cw source at 3.3  $\mu$ m generated by difference-frequency generation in periodically poled lithium niobate of two near-IR tunable diode lasers, Chen and co-workers at the National Institute of Standards and Technology<sup>34</sup> were able to achieve reproducibility of ~16‰ for  $\delta\text{D}$  using tens of millibars pressure and a 36-m path-length cell. Preconcentration of sampled methane by a factor of ~800 was needed and was achieved through cryogenic trapping, with methane extracted from ~25 of air.

### 4. Application to Mars

We concluded above that *in situ* measurement of atmospheric CH<sub>4</sub> on the surface of Mars must be made to better than 1-ppbv accuracy, and preferably to 0.1 ppbv. Also, to provide a basic distinction between biogenic and abiogenic sources on Mars, isotope ratios in methane would have to be made to better than 10‰ for  $\delta^{13}\text{C}$  and to better than 50‰ for  $\delta\text{D}$ . So how can this be done for an atmosphere containing very little methane (~10 ppbv) to begin with?

We begin by imposing constraints on a potential *in situ* laser spectrometer. Although very long path lengths (kilometers) are desirable, we need to begin with a reasonable, easily achieved, optical path length (say, 40 m) that can be reliably maintained in the Mars environment. Such a path can be readily provided by multipass Herriott<sup>47</sup> or astigmatic<sup>48</sup> cells, whether open path or closed cells. The difficulty of the isotope ratio in particular forces us to rely on only the strongest absorption features near 3.3  $\mu$ m that we would access using a single-device TE-cooled TDL as described above. A simulated spectrum in the region of strong <sup>12</sup>CH<sub>4</sub> is shown in Fig. 3. This region is so rich in lines that we can take advantage of the line density (all easily resolved by a scanning TDL spectrometer) to increase the sensitivity. The group of approximately eight of the strongest lines (Fig. 3) produces an absorption equivalent to a single line of depth of ~1 × 10<sup>-3</sup>, or 0.1%, for 10-ppbv methane. For integration times of minutes, it is reasonable to



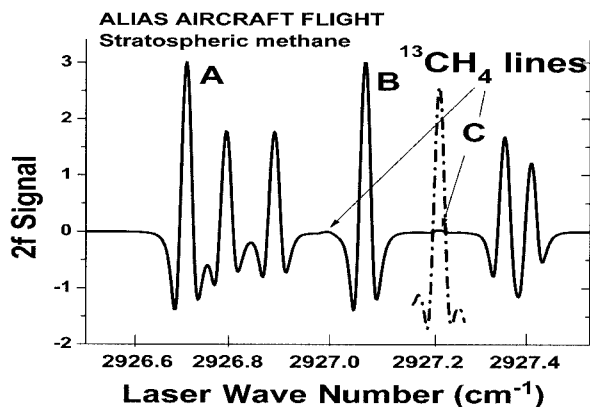


Fig. 4. Second-harmonic absorption spectrum recorded by the ALIAS instrument during a flight in 1999 (previously unpublished) through Earth's stratosphere, showing strong line features of  $^{12}\text{CH}_4$  (lines A, B) with an excellent signal-to-noise ratio, and also weaker  $^{13}\text{CH}_4$  lines identified by arrows. The second  $^{13}\text{CH}_4$  line (line C) is also shown expanded by 100 in the y axis for clarity.

expect our spectrometer to have a minimum-detectable absorption of  $1 \times 10^{-5}$ , so our minimum detectable  $\text{CH}_4$  amount will be 0.1 ppbv. If indeed we observe  $\approx 10$  ppbv in the atmosphere, we would expect a precision of 0.1 ppbv on our measurement. Absolute accuracy should be better than 3% with careful calibration and reasonable measurement of pressure (1%) and temperature (5 K). We note that these lines are not very temperature sensitive.

For isotopic measurements, we first consider  $^{13}\text{CH}_4$ . We assess the needs for achieving the goal of measuring  $\delta^{13}\text{C}$  to  $\sim 10\text{‰}$  from three sources: a combination of earlier actual measurements and calculations based on minimum-detectable absorption levels.

(i) Bergamaschi *et al.*<sup>21–23</sup> achieved a reproducibility of  $\sim 0.5\text{‰}$  and a precision of  $\sim 0.2\text{‰}$  for a 15-min sample in a 213-m path needing at least 50-ppmv methane ( $^{12}\text{CH}_4$ ) at pressures of 30 mbars so that, at  $3008\text{ cm}^{-1}$ , line-center absorptions of  $\sim 10\%$  were necessary for this high precision. Therefore, for our target precision of  $\sim 10\text{‰}$ , smaller line-center absorptions of  $\sim 3 \times 10^{-3}$  are needed. Calculations show that with a 40-m path, these line-center absorptions can be reached at a 40-mbar total pressure with  $\sim 5$ -ppmv methane.

(ii) The ALIAS aircraft measurements (Fig. 4) of lines in a different region (P branch) of the band provided ratios of observed line intensities to assess precision. In a 30-min average of spectra recorded every second,  $\delta^{13}\text{C}$  could be measured to a precision of  $\sim 5\text{‰}$  (or  $10\text{‰}$  in 15 min) with 2-ppmv methane in an 80-m path. Therefore this suggests that in a 40-m path, at least 4-ppmv methane is needed. We note that when there is a large difference in line intensity, the precision of the ratio of two lines (C and B in Fig. 4) is driven by the weakest ( $^{13}\text{CH}_4$ ) line. Ratioing two strong  $^{12}\text{CH}_4$  lines (A and B in Fig. 4) produced a precision of  $0.2\text{‰}$  in the 30-min period, showing the

capability for methane detection and measurement.

(iii) We would begin direct calculations by assuming that a minimum-detectable line center absorption of  $1 \times 10^{-5}$  could be achieved in 15 min. For 10% measurement precision, minimum line-center absorption levels of  $\sim 1 \times 10^{-3}$  would be needed. Calculations show that with a 40-m path, and say 40-mbar total pressure, these absorption levels need nearly 2-ppmv methane.

From these three studies, we estimate that, to measure  $\delta^{13}\text{C}$  to  $10\text{‰}$  using a 40-m path with a sample pressure of tens of millibars, methane amounts of  $\sim 3 \pm 2$  ppmv are required. We note that for  $\delta^{13}\text{C}$  measurements in  $\text{CO}_2$  where similar size isotopic lines and large amounts of  $\text{CO}_2$  are available,  $\delta^{13}\text{C}$  should be measurable to  $0.2\text{‰}$ , as shown in the ALIAS precision in paragraph (ii) above.

The scientific requirements for measuring  $\text{CH}_3\text{D}$  mean that the needed precision is much less. Although  $\text{CH}_3\text{D}$  line strengths are often inherently stronger than those of  $^{13}\text{CH}_4$  (see Fig. 2), the abundance of  $\text{CH}_3\text{D}$  (0.06% of methane) is 18 times lower than that of  $^{13}\text{CH}_4$  (1.1%), so the  $\text{CH}_3\text{D}$  lines have less line-center absorptions. For  $\delta\text{D}$  in methane, Chen *et al.*<sup>34</sup> achieved an uncertainty of  $\sim 16\text{‰}$  in their 36-m path after preconcentration by a factor of 800–1400 ppmv using relatively weak lines. This study would suggest that 50% precision could be achieved with  $\sim 500$ -ppmv methane, or  $\sim 300$  ppmv with stronger lines. Bergamaschi *et al.*<sup>23</sup> achieved reproducibility for  $\delta\text{D}$  of  $2\text{‰}$  with 2000 ppmv in a 213-m path. Therefore, in a 40-m path, reproducibility of  $\sim 50\text{‰}$  would be achieved with 400-ppmv methane. Direct calculation for a 36-m path and 40-mbar pressure (somewhat higher than Mars ambient pressure near 7–10 mbars, but easily achieved in a closed cell) also shows that  $\approx 400$ -ppmv methane would be needed. Therefore from these three studies we estimate that to measure  $\delta\text{D}$  to  $\sim 50\text{‰}$  on Earth at 10 ppbv would require  $\approx 400 \pm 100$ -ppmv methane.

For Mars, measurement of  $\text{CH}_3\text{D}$  and ultimately the precision needed to determine  $\delta\text{D}$  to  $\sim 50\text{‰}$  is greatly helped by two factors. First, because the D/H ratio is  $\sim 5$  times that of Earth, we expect there to be nominally five times as much  $\text{CH}_3\text{D}$ , translating to IR absorption lines with five times the intensity. Second, Yung *et al.*<sup>49</sup> report that, because of the diminished rate of reaction of OH with  $\text{CH}_3\text{D}$  compared with its reaction with  $\text{CH}_4$ , the lifetime of  $\text{CH}_3\text{D}$  could be up to twice that of  $\text{CH}_4$ , or  $\approx 60$  years, doubling the steady-state concentration of  $\text{CH}_3\text{D}$  on Mars. These two factors result in a possible increase of approximately ten in  $\text{CH}_3\text{D}$  amounts, and therefore the size of the expected absorption lines. Therefore we estimate that to measure  $\delta\text{D}$  to  $\sim 50\text{‰}$  on Mars would require  $\sim 40 \pm 10$ -ppmv methane.

With only 10 ppbv available, preconcentration of Mars atmosphere by a factor of  $\sim 300$ –3 ppmv will be required to measure  $\delta^{13}\text{C}$  to  $10\text{‰}$ ; for  $\delta\text{D}$  (to  $\sim 50\text{‰}$ ), preconcentration by a factor of  $\sim 4000$ –40 ppmv will be required (see Table 2). Sample preconcentration is

**Table 3. Mass Estimate of Laser Spectrometer for Mars Methane**

| Part Description   | Mass (g) |
|--|----------|
| Sample cell (2.5-cm-diameter mirrors in 20-cm-long cell, support struts, insulation) | 100      |
| Cell mirrors and end caps  | 40       |
| TE cooler, laser, detector, lenses, mounts   | 40       |
| Electronics board with TE driver   | 45       |
| Electrical cabling   | 40       |
| Pressure transducer  | 10       |
| Mass margin (30%)  | 85       |
| Total  | 360      |

routinely used in many analytical chemistry techniques and has been applied to methane isotopic measurements. Liquid cryogen trapping, as used by Chen *et al.*,<sup>34</sup> will not be possible on Mars. Cooling capability for preconcentration will be limited to available long-life, reliable thermoelectric or stirling cycle coolers specifically developed for planetary missions. Preconcentration of methane could be achieved by a combination of cooling and scrubbing of other gases, most notably CO<sub>2</sub> for Mars application.

This analysis would not be complete without including a discussion of increased path length as a way to offset the need for preconcentration, especially in light of new developments in cavity ring-down spectroscopy, a technique that in principle provides high sensitivity as a result of increased path length.<sup>50</sup> It is my opinion, however, that the final sensitivity of this approach is no better than the standard second-harmonic detection techniques because, from a direct absorption spectrum, the sensitivity increase from a much larger path length is approximately the same as that from second-harmonic detection. Dahnke *et al.*<sup>35</sup> reported measurements of CH<sub>4</sub> and its isotope ratio measurements for <sup>13</sup>C/<sup>12</sup>C using mid-IR (2947–3050-cm<sup>-1</sup>) cavity leak-out spectroscopy, a modification of cavity ring-down spectroscopy. In 20 s, using a ring-down path length of 3.6 km, they achieved a detection limit of 0.105-ppbv CH<sub>4</sub> in air at 50-mbars, the same detection limit achieved for standard second-harmonic detection in a 40-m path, as reported here. In a 2-min period,  $\delta^{13}\text{C}$  was measured to 11‰ for a sample containing 1.962 ppmv, a result again in concert with the needs (~3 ppmv) for the

standard second-harmonic technique presented in this study.

On the basis of our earlier design of a miniature Mars laser hygrometer<sup>36</sup> for water-vapor measurements that weighed 230 g total, we can estimate the specifications for a Mars laser spectrometer for CH<sub>4</sub> with  $\delta^{13}\text{C}$  capability. First, the flight-developed electronics board for a single laser at 3.3  $\mu\text{m}$  (45 g) would be used, requiring regulated 5-V and  $\pm 15\text{-V}$  supply voltages. The power draw would be approximately 5-W at start-up and 3-W continuous during measurements. A 36-m path-length multipass cell of the Herriott or astigmatic cell design with a base path of ~20 cm could be used. Total mass of the instrument with some margin is estimated by weighing prototype parts to be  $\approx 360$  g (see Table 3). Required data rates per measurement would range from 2058 bytes for the full spectral scan to be transmitted to only 40 bytes if processed onboard (see Table 4 and discussion in Ref. 34).

In conclusion, with a simple stand-alone tunable laser spectrometer we would be able to measure total methane amounts of 0.1 ppbv in the Martian atmosphere, using either an open-path multipass cell or in an enclosed cell sampling the atmosphere under control. However, for methane isotope ratios, the tunable laser spectrometer would need additional gas handling and processing capability for preconcentration of atmospheric samples prior to measurement. This could readily be done with a combination of cooling and CO<sub>2</sub> scrubbing techniques. With preconcentration as part of a Martian on-surface chemistry laboratory or suite of instruments, we could readily measure the  $\delta^{13}\text{C}$  content of methane to 10‰ using tunable laser absorption in a standard 36-m path-length sample cell. However, even in a cell of a considerably longer path, measurements of  $\delta\text{D}$  at the required minimum precision level of 50‰ will be difficult by use of *in situ* tunable laser spectroscopy, despite the higher relative abundances of CH<sub>3</sub>D on Mars compared with Earth; path lengths of several hundreds of meters will be needed. The distribution of methane on Mars is unknown, so the need to preconcentrate may be removed or at least mitigated by the discovery of gradients in methane abundance, for example, near the source, whether from hydrothermal vents, comet impact regions, or bacterial colonies.

Finally, a strategy to assess the biogenic origin or otherwise of the methane observed on Mars has to be done in concert with careful measurements of CH<sub>4</sub>,

**Table 4. Data Rate Inventories for an Entire Spectral Scan and an Onboard Processed Scan**

| Entire Spectral Scan         | Bytes | Processed Spectral Scan         | Bytes |
|------------------------------|-------|---------------------------------|-------|
| 512 points (direct spectrum) | 1024  | 5 points in the direct spectrum | 10    |
| 512 points (2f spectrum)     | 1024  | 5 points in the 2f spectrum     | 10    |
|                              |       | Indices of these 5 points       | 10    |
| Pressure and temperature     | 8     | Pressure and temperature        | 8     |
| 5-V sense line               | 2     | 5-V sense line                  | 2     |
| Total                        | 2058  | Total                           | 40    |



$^{13}\text{CH}_4$ , and  $\text{CH}_3\text{D}$  in addition to simultaneous measurements of  $^{13}\text{CO}_2$  and  $\text{CO}_2$  and of  $\text{H}_2\text{O}$  and  $\text{HDO}$ .

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